

We claim:

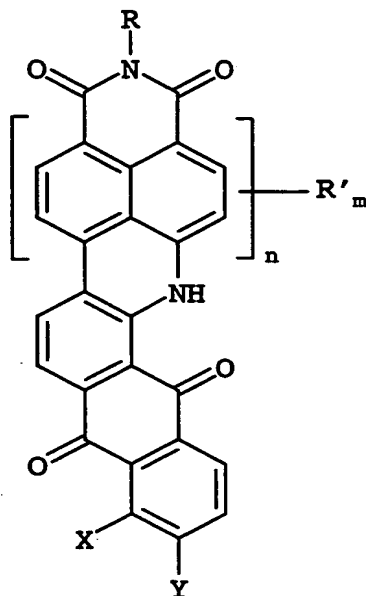
1. A rylene dye of the general formula I

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15

20



I

where the variables are defined as follows:

25

R is hydrogen;

30

C₁-C₃₀-alkyl whose carbon chain may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by carboxyl, sulfo, hydroxyl, cyano, C₁-C₆-alkoxy and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;

35

C₅-C₈-cycloalkyl whose carbon framework may be interrupted by one or more -O-, -S- and/or -NR¹- moieties and may be mono- or polysubstituted by C₁-C₆-alkyl;

40

aryl or hetaryl which may each be mono- or polysubstituted by C₁-C₁₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano, carboxyl, -CONHR², -NHCOR² and/or aryl- or hetarylazo, each of which may be substituted by C₁-C₁₀-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano and/or carboxyl;

45

R' is bromine; cyano; $-NR^3_2$;

aryloxy, arylthio, hetaryloxy or hetarylthio, each of which may be mono- or polysubstituted by C_1 - C_{12} -alkyl, C_1 - C_{12} -alkoxy, cyano, $-CONHR^2$ and/or $-NHCOR^2$;

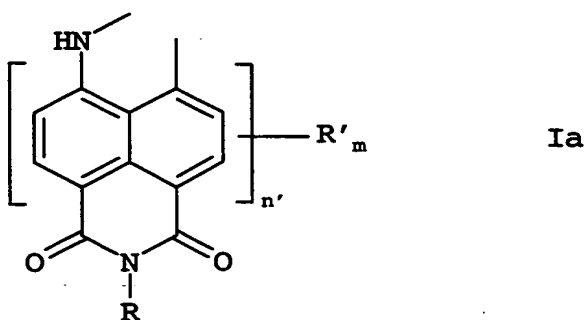
C_3 - C_{18} -alk-1-ynyl whose carbon chain may be interrupted by one or more $-O-$, $-S-$, $-NR^1-$, $-CO-$ and/or $-SO_2-$ moieties and may be mono- or polysubstituted by $-COOR^1$, $-SO_3R^1$, hydroxyl, cyano, C_1 - C_6 -alkoxy, C_5 - C_8 -cycloalkyl, aryl and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;

R^1 is hydrogen or C_1 - C_6 -alkyl;

R^2 is hydrogen; C_1 - C_{18} -alkyl; aryl or hetaryl, each of which may be substituted by C_1 - C_8 -alkyl, C_1 - C_6 -alkoxy, halogen, hydroxyl and/or cyano;

R^3 is hydrogen; C_1 - C_{18} -alkyl; aryl or hetaryl, each of which may be substituted by C_1 - C_8 -alkyl, C_1 - C_6 -alkoxy, halogen, hydroxyl and/or cyano; both R^3 radicals may be joined to give a 5- to 7-membered heterocyclic radical which contains the nitrogen atom and is bonded via it;

X, Y are both hydrogen or bonded together to form a six-membered ring in a radical of the formula Ia



where X is the $-NH-$ group and Y is the other free chemical bond;

n is 2, 3, 4 or additionally 1 when X and Y are a radical of the formula Ia;

n' is from 1 to 4;

m is from 0 to 6.

5 2. A rylene dye of the formula I as claimed in claim 1, where the variables are defined as follows:

10 R is C₁-C₃₀-alkyl whose carbon chain may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by hydroxyl, cyano, C₁-C₆-alkoxy and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;

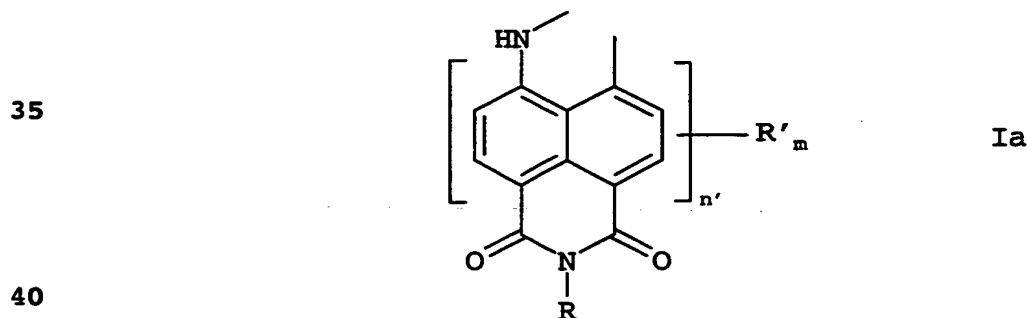
15 aryl or hetaryl which may each be mono- or polysubstituted by C₁-C₁₈-alkyl, C₁-C₆-alkoxy, hydroxyl, cyano, -CONHR² and/or -NHCOR²;

20 R' is bromine or aryloxy which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₆-alkoxy and/or cyano;

R¹ is hydrogen or C₁-C₆-alkyl;

25 R² is hydrogen; C₁-C₁₈-alkyl; aryl or hetaryl, each of which may be substituted by C₁-C₈-alkyl, C₁-C₆-alkoxy and/or cyano;

30 X, Y are both hydrogen or bonded together to form a six-membered ring in a radical of the formula Ia



where X is the -NH- group and Y is the other free chemical bond;

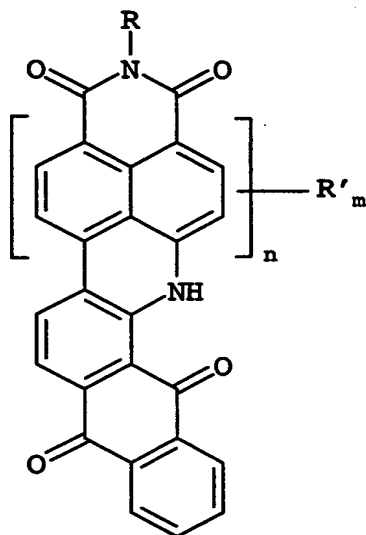
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n is 2, 3, 4 or additionally 1 when X and Y are a radical of the formula Ia;

n' is from 1 to 4;

m is from 0 to 6.

3. A process for preparing rylene dyes of the general formula I'



I'

where the variables are defined as follows:

R is hydrogen;

C₁-C₃₀-alkyl whose carbon chain may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by carboxyl, sulfo, hydroxyl, cyano, C₁-C₆-alkoxy and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;

C₅-C₈-cycloalkyl whose carbon framework may be interrupted by one or more -O-, -S- and/or -NR¹- moieties and may be mono- or polysubstituted by C₁-C₆-alkyl;

aryl or hetaryl which may each be mono- or polysubstituted by C₁-C₁₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano, carboxyl, -CONHR², -NHCOR² and/or aryl- or hetarylazo, each of which may be substituted by C₁-C₁₀-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano or carboxyl;

R' is bromine; cyano; $-NR^3_2$;

aryloxy, arylthio, hetaryloxy or hetarylthio, each of which may be mono- or polysubstituted by C_1 - C_{12} -alkyl, C_1 - C_{12} -alkoxy, cyano, $-CONHR^2$ and/or $-NHCOR^2$;

C_3 - C_{18} -alk-1-ynyl whose carbon chain may be interrupted by one or more $-O-$, $-S-$, $-NR^1-$, $-CO-$ and/or $-SO_2-$ moieties and may be mono- or polysubstituted by $-COOR^1$, $-SO_3R^1$, hydroxyl, cyano, C_1 - C_6 -alkoxy, C_5 - C_8 -cycloalkyl, aryl and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;

R¹ is hydrogen or C_1 - C_6 -alkyl;

R² is hydrogen; C_1 - C_{18} -alkyl; aryl or hetaryl, each of which may be substituted by C_1 - C_8 -alkyl, C_1 - C_6 -alkoxy, halogen, hydroxyl or cyano;

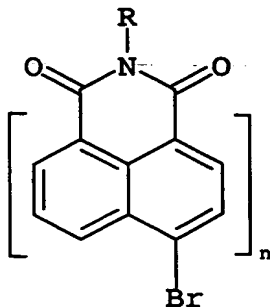
R³ is hydrogen; C_1 - C_{18} -alkyl; aryl or hetaryl, each of which may be substituted by C_1 - C_8 -alkyl, C_1 - C_6 -alkoxy, halogen, hydroxyl and/or cyano; both R³ radicals may be joined to give a 5- to 7-membered heterocyclic radical which contains the nitrogen atom and is bonded via it;

n is 2, 3 or 4;

m is from 0 to 6,

which comprises

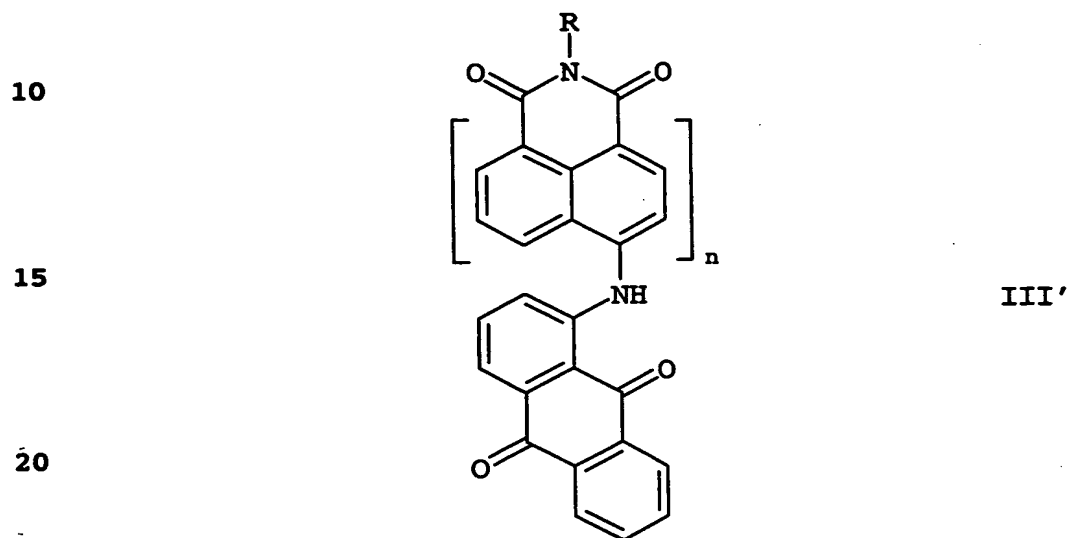
a) reacting a rylene derivative monobrominated in the peri-position of the general formula II'



II'

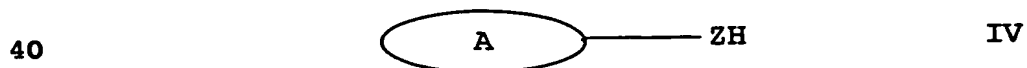
with 1-aminoanthraquinone in a cross-coupling reaction in the presence of an aprotic organic solvent, of a transition metal catalyst system and of a base,

- 5 b) cyclizing the rylenanthramine formed in step a) of the general formula III'



25 in the presence of a polar organic solvent and of a base to give the rylene dye of the formula I' which is unsubstituted in the rylene core and where m is 0, and

- 30 c) if desired, converting the rylene dye I' unsubstituted in the rylene core and obtained in step b) to the rylene dye of the formula I' brominated in the rylene core where R' is bromine and m does not equal 0 by reacting with elemental bromine, and
- 35 d) if desired, converting the rylene dye I' brominated in the rylene core and obtained in step c)
- d1) by reacting with a compound of the general formula IV



45 where Z is sulfur or oxygen and the ring A is an aryl or hetaryl radical, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR²,

in the presence of an inert nitrogen-basic organic solvent and of a base to give the rylene dye of the formula I' which is substituted in the rylene core and where R' is aryloxy, arylthio, hetaryloxy or hetarylthio, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR², and m does not equal 0,

d2) by reacting with copper(I) cyanide in the presence of a dipolar aprotic organic solvent to give the rylene dye of the formula I' which is substituted in the rylene core and where R' is cyano and m does not equal 0,

d3) by reacting with an alkyne of the general formula V



where R'' is a C₁-C₁₆-alkyl radical which may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by -COOR¹, -SO₃R¹, hydroxyl, cyano, C₁-C₆-alkoxy, C₅-C₈-cycloalkyl, aryl and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic,

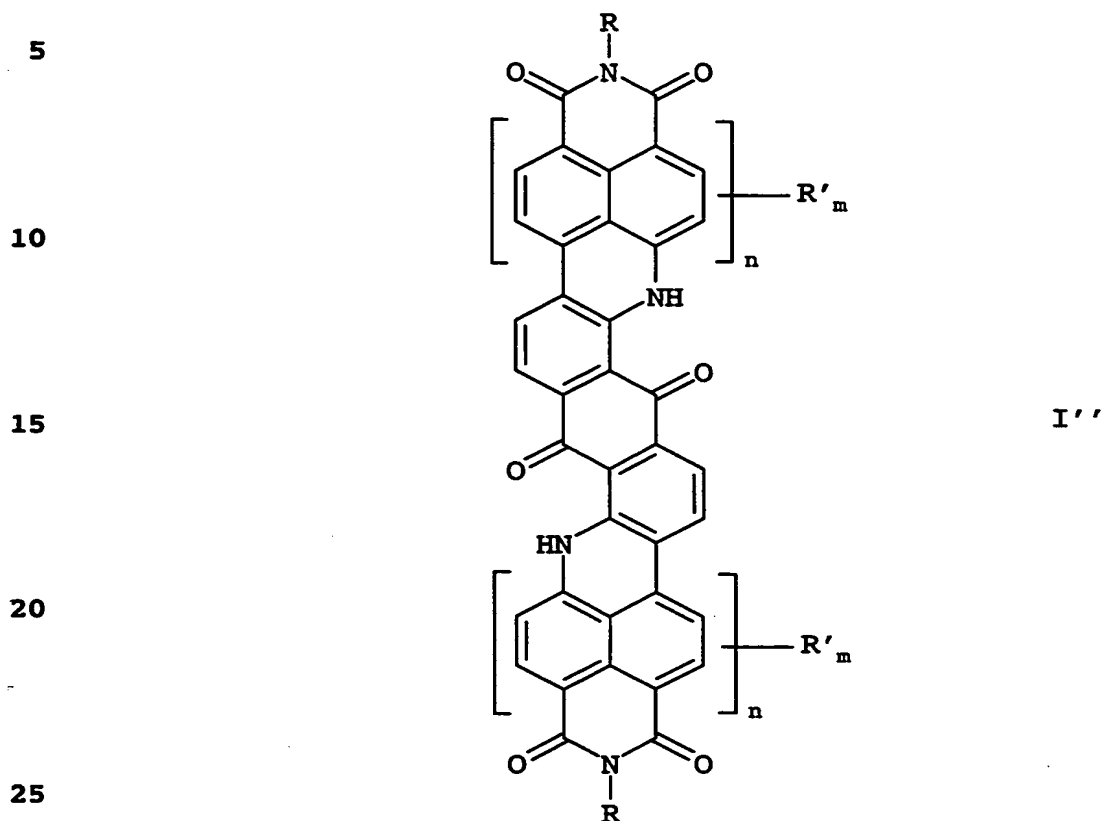
in the presence of an aprotic organic solvent, of a palladium complex as a catalyst, of a copper salt as a cocatalyst and of a base to give the rylene dye of the formula I' which is substituted in the rylene core and where R' is -C≡C-R'' and m does not equal 0, or

d4) by reacting with ammonia or an amine of the general formula VI



in the presence of a dipolar aprotic organic solvent to give the rylene dye of the formula I' which is substituted in the rylene core and where R' is -NR³₂ and m does not equal 0.

4. A process for preparing symmetrical rylene dyes of the general formula I''



where the variables are defined as follows:

R is hydrogen;

C₁-C₃₀-alkyl whose carbon chain may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by carboxyl, sulfo, hydroxyl, cyano, C₁-C₆-alkoxy and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;

C₅-C₈-cycloalkyl whose carbon framework may be interrupted by one or more -O-, -S- and/or -NR¹- moieties and may be mono- or polysubstituted by C₁-C₆-alkyl;

aryl or hetaryl which may each be mono- or polysubstituted by C₁-C₁₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano, carboxyl, -CONHR², -NHCOR² and/or aryl- or hetarylazo, each of which may be substituted by

C₁-C₁₀-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano and/or carboxyl;

R' is bromine; cyano; -NR³₂;

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aryloxy, arylthio, hetaryloxy or hetarylthio, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR²;

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C₃-C₁₈-alk-1-ynyl whose carbon chain may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by -COOR¹, -SO₃R¹, hydroxyl, cyano, C₁-C₆-alkoxy, C₅-C₈-cycloalkyl, aryl and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;

15

R¹ is hydrogen or C₁-C₆-alkyl;

20

R² is hydrogen; C₁-C₁₈-alkyl; aryl or hetaryl, each of which may be substituted by C₁-C₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl and/or cyano;

25

R³ is hydrogen; C₁-C₁₈-alkyl; aryl or hetaryl, each of which may be substituted by C₁-C₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl and/or cyano; both R³ radicals may be joined to give a 5- to 7-membered heterocyclic radical which contains the nitrogen atom and is bonded via it;

30

n is 1, 2, 3 or 4;

m is from 0 to 6,

which comprises

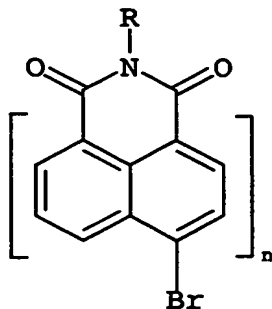
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a) reacting a rylene derivative monobrominated in the peri-position of the general formula II'

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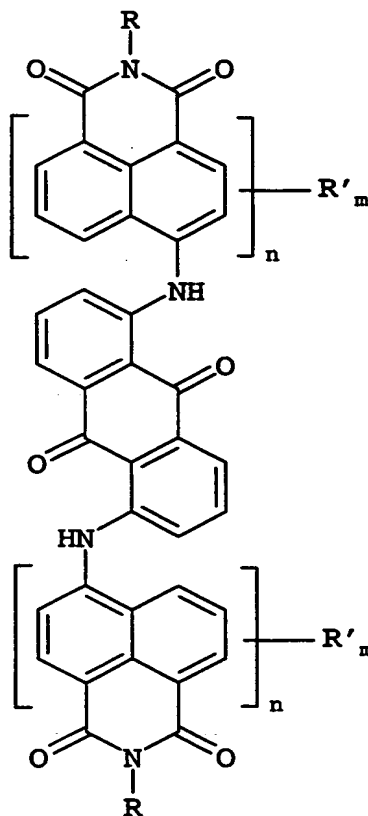
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II'

with 1,5-diaminoanthraquinone in a double cross-coupling reaction in the presence of an aprotic organic solvent, of a transition metal catalyst system and of a base,

- b) cyclizing the rylenanthramine formed in step a) of the general formula III''



III''

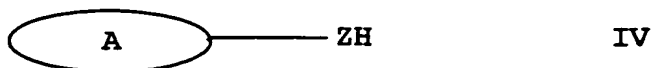
in the presence of a polar organic solvent and of a base to give the rylene dye of the formula I'' where m is 0, and

- c) if desired, converting the rylene dye I' unsubstituted in the rylene core and obtained in step b) to the rylene dye of the formula I'' brominated in the rylene core where R'

is bromine and m is equal to 0 by reacting with elemental bromine, and

d) if desired, converting the rylene dye I'' brominated in the rylene core and obtained in step c)

d1) by reacting with a compound of the general formula IV



where Z is sulfur or oxygen and the ring A is an aryl or hetaryl radical, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR²,

in the presence of an inert nitrogen-basic organic solvent and of a base to give the rylene dye of the formula I'' which is substituted in the rylene core and where R' is aryloxy, arylthio, hetaryloxy or hetarylthio, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR², and m does not equal 0,

d2) by reacting with copper(I) cyanide in the presence of a dipolar aprotic organic solvent to give the rylene dye of the formula I'' which is substituted in the rylene core and where R' is cyano and m does not equal 0,

d3) by reacting with an alkyne of the general formula V

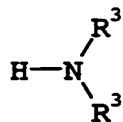


where R'' is a C₁-C₁₆-alkyl radical which may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by -COOR¹, -SO₃R¹, hydroxyl, cyano, C₁-C₆-alkoxy, C₅-C₈-cycloalkyl, aryl and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic,

in the presence of an aprotic organic solvent, of a palladium complex as a catalyst, of a copper salt as a cocatalyst and of a base to give the rylene dye of the

formula I'' which is substituted in the rylene core and where R' is $-C\equiv C-R''$ and m does not equal 0, or

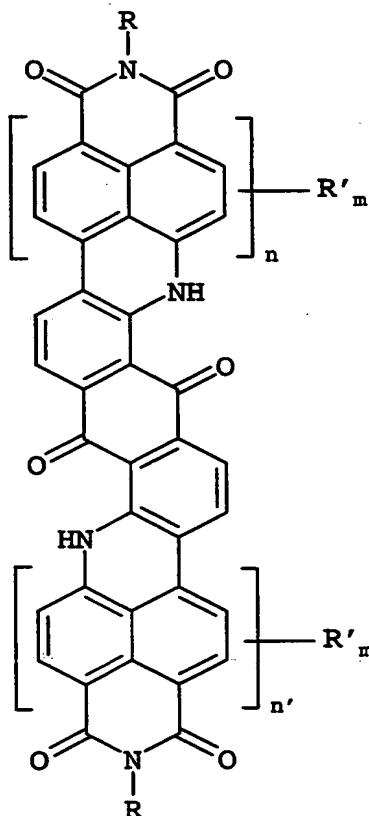
d4) by reacting with ammonia or an amine of the general formula VI



VI

in the presence of a dipolar aprotic organic solvent to give the rylene dye of the formula I'' which is substituted in the rylene core and where R' is $-NR^3_2$ and m does not equal 0.

5. A process for preparing nonsymmetrical rylene dyes of the general formula I'''



I'''

where the variables are defined as follows:

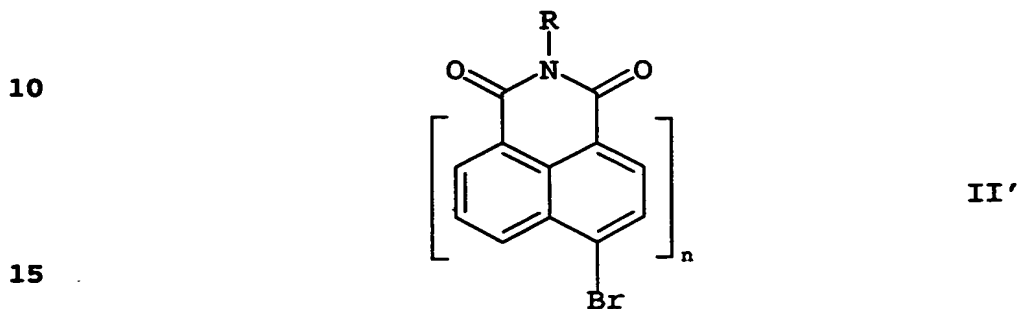
R is hydrogen;

- 5 C₁-C₃₀-alkyl whose carbon chain may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by carboxyl, sulfo, hydroxyl, cyano, C₁-C₆-alkoxy and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;
- 10 C₅-C₈-cycloalkyl whose carbon framework may be interrupted by one or more -O-, -S- and/or -NR¹- moieties and may be mono- or polysubstituted by C₁-C₆-alkyl;
- 15 aryl or hetaryl which may each be mono- or polysubstituted by C₁-C₁₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano, carboxyl, -CONHR², -NHCOR² and/or aryl- or hetarylazo, each of which may be substituted by C₁-C₁₀-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl, cyano and/or carboxyl;
- 20 R' is bromine; cyano; -NR³₂;
- aryloxy, arylthio, hetaryloxy or hetarylthio, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR²;
- 25 C₃-C₁₈-alk-1-ynyl whose carbon chain may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by -COOR¹, -SO₃R¹, hydroxyl, cyano, C₁-C₆-alkoxy, C₅-C₈-cycloalkyl, aryl and/or a 5- to 7-membered heterocyclic radical which
- 30 is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic;
- R¹ is hydrogen or C₁-C₆-alkyl;
- 35 R² is hydrogen; C₁-C₁₈-alkyl; aryl or hetaryl, each of which may be substituted by C₁-C₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl and/or cyano;
- 40 R³ is hydrogen; C₁-C₁₈-alkyl; aryl or hetaryl, each of which may be substituted by C₁-C₈-alkyl, C₁-C₆-alkoxy, halogen, hydroxyl and/or cyano; both R³ radicals may be joined to give a 5- to 7-membered heterocyclic radical which contains the nitrogen atom and is bonded via it;
- 45 n, n' are each 1, 2, 3 or 4, and n ≠ n';

m is from 0 to 6,

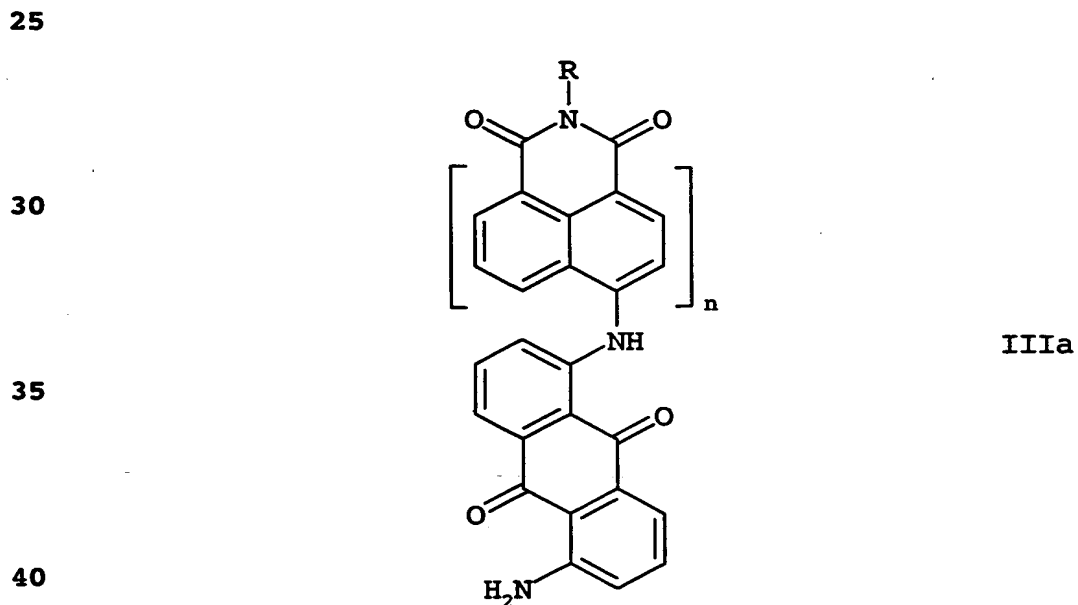
which comprises

- 5 a1) initially reacting a rylene derivative monobrominated in the peri-position of the general formula II'



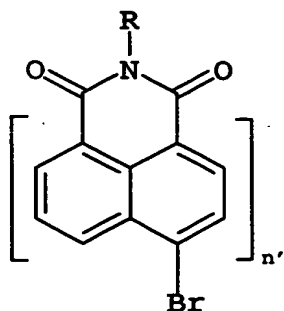
20 with excess 1,5-diaminoanthraquinone in a first cross-coupling reaction in the presence of an aprotic organic solvent, of a transition metal catalyst system and of a base,

- 25 a2) reacting the aminorylenanthramine obtained in step a) of the general formula IIIa



45 with a rylene derivative monobrominated in the peri-position of the general formula II''

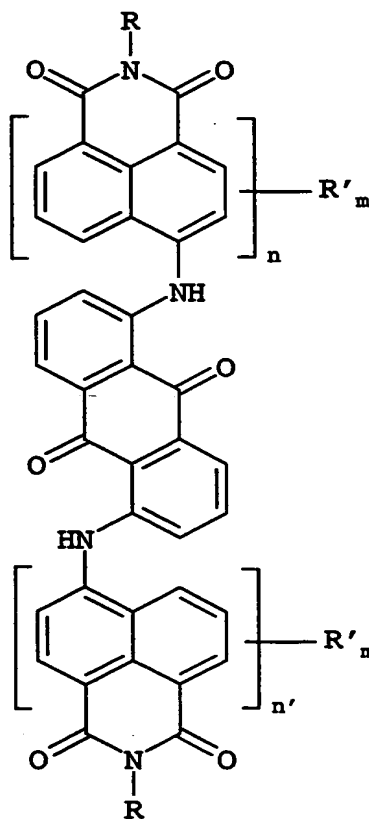
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II''

in the presence of an aprotic organic solvent, of a transition metal catalyst and of a base in a second cross-coupling reaction,

- b) cyclizing the ryleneanthramine formed in step a) of the general formula III'''



III'''

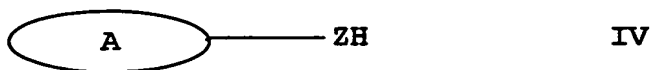
in the presence of a polar organic solvent and of a base to give the rylene dye of the formula I''' which is unsubstituted in the rylene core and where m is 0, and

- c) if desired, converting the rylene dye I''' unsubstituted in the rylene core and obtained in step b) to the rylene dye of the formula I''' brominated in the rylene core

where R' is bromine and m does not equal 0 by reacting with elemental bromine, and

d) if desired, converting the rylene dye I''' brominated in the rylene core and obtained in step c)

d1) by reacting with a compound of the general formula IV



where Z is sulfur or oxygen and the ring A is an aryl or hetaryl radical, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR²,

in the presence of an inert nitrogen-basic organic solvent and of a base to give the rylene dye of the formula I''' which is substituted in the rylene core and where R' is aryloxy, arylthio, hetaryloxy or hetarylthio, each of which may be mono- or polysubstituted by C₁-C₁₂-alkyl, C₁-C₁₂-alkoxy, cyano, -CONHR² and/or -NHCOR², and m does not equal 0,

d2) by reacting with copper(I) cyanide in the presence of a dipolar aprotic organic solvent to give the rylene dye of the formula I''' which is substituted in the rylene core and where R' is cyano and m does not equal 0,

d3) by reacting with an alkyne of the general formula V

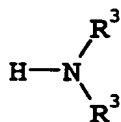


where R'' is a C₁-C₁₆-alkyl radical which may be interrupted by one or more -O-, -S-, -NR¹-, -CO- and/or -SO₂- moieties and may be mono- or polysubstituted by -COOR¹, -SO₃R¹, hydroxyl, cyano, C₁-C₆-alkoxy, C₅-C₈-cycloalkyl, aryl and/or a 5- to 7-membered heterocyclic radical which is bonded via a nitrogen atom and may contain further heteroatoms and be aromatic,

in the presence of an aprotic organic solvent, of a palladium complex as a catalyst, of a copper salt as a cocatalyst and of a base to give the rylene dye of the

formula I''' which is substituted in the rylene core and where R' is $-C\equiv C-R''$ and m does not equal 0, or

d4) by reacting with ammonia or an amine of the general formula VI



VI

in the presence of a dipolar aprotic organic solvent to give the rylene dye of the formula I''' which is substituted in the rylene core and where R' is $-NR^3_2$ and m does not equal 0.

6. The use of rylene dyes of the general formula I as claimed in claim 1 or 2 for coloring high molecular weight organic and inorganic materials.
7. The use as claimed in claim 6, wherein plastics, paints, printing inks and oxidic layer systems are colored.
8. The use of rylene dyes of the general formula I as claimed in claim 1 or 2 as dispersants, pigment additives for organic pigments and intermediates for the preparation of pigment additives.
9. The use of rylene dyes of the general formula I as claimed in claim 1 or 2 for producing aqueous polymer dispersions which are colored or absorb in the near infrared region of the electromagnetic spectrum.
10. The use of rylene dyes of the general formula I as claimed in claim 1 or 2 as photoconductors in electrophotography.